BATCH STUDY REMOVAL OF COPPER IONS FROM WATER BY USING ION EXCHANGE RESIN

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CERTIFICATE

This is to certify that the work in this term paper entitled **"Batch Study removal of copper ions from water by ion exchange resin"** submitted by **Shilpi Das** in partial fulfillments for her requirements for the award of Master of Technology Degree in Chemical Engineering session 2012-14 at National Institute of Technology, Rourkela has been carried out under my supervision and guidance. To the best of my knowledge the matter embodied in the thesis is her bona fide work.

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ABSTRACT

Copper is a highly toxic metal which is found as pollutant in water that is mainly originating from chemical manufacturing, painting, coating & other industries etc. In this study the copper ions has been removed from water by using an ion exchange resin Tulsion A-23 by the adsorption process. It is the most attractive option due to the avaibility of cost effective, sustainable & eco-friendly bioadsorbents. Aim of the experiment is to study the effect of various parameters such as contact time, pH of solution, initial adsorbate concentration, initial metal ion concentration & temperature on the sorption & optimize their values. Experimental results have shown that resin had a good adsorption capacity for copper and has the capability to reduce the concentration of copper in waste water. Suitable time for the operation is found to be 90min at solution pH of 6.86 with 1g/L of resin and initial concentration of copper 10mg/L. Removal of copper at these optimized parameter is found to be 98.76%. After that the removal of copper became very slow. The experimental data is well fitted with Temkin adsorption isotherm & follows second order kinetics. Based on these results we can conclude that it is possible to use this resin for removing copper from water.

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Nomenclature:

USEPA	U.S. Environmental Protection Agency
WHO	World Health Organization
CEPT	Chemically enhanced primary treatment
NF	Nanofiltration
C_0	Initial metal ion concentration (mg/L)
C_i	Final metal ion concentration in the solution (mg/L)
q	Amount of copper adsorbed(mg/g)

Ce	the equilibrium concentration of copper in solution (mg/L),
k_1	Rateconstant Of the pseudo-first-order adsorption (min^{-1})
q_e	uptake capacity
b	Langmuir isotherm constant that relates to the energy of adsorption (L/mg)

CHAPTER 1

INTRODUCTION

Introduction

1.1 Preamble:-

Water is necessary for endurance of living organisms on aquatic as well as at global ecosystem. It is used for many purposes which include domestic, cultivation and industrial uses. Its increasing globe of effectiveness has loaded it with number of pollutants, one among them are metallic pollutants. Metallic pollutants are non biodegradable due to which water is polluted with metallic pollutants finds its way into streams as wastewater.

Pollution caused by heavy metal in wastewater is a recognizable ecological peril, since the poisonous metal ions dissolved can reach the top of the food chain and thus become a peril issue for human health. They have atomic density more than 6 g per cm^3.Heavy metals such as arsenic, copper, cadmium, chromium, nickel, zinc, lead, mercury reserves because of their contaminated, non ecological &relentless nature. Toxic heavy metal infectivity of industrialized waste water is a common environmental trouble. Federal & local agencies have therefore predetermined expulsion limits on the levels of these heavy metals in the wastes being quitted in the environment. Among heavy metals, copper is an important heavy metal present in the aquatic environment.It is an important engineering material with wide industrial applications and is an essential factor for animal metabolism.

Cu (II) and copper containing materials have number of applications such as a supplement in cattle feed, for manufacturing of copper water pipes and brass radiators, as a constituent of fertilizers, pesticides, fireworks and antifouling paints applied on ship hulls. Copper enters into the environment through sources such as natural and anthropogenic. The contagion of air and water, by copper is contributed from the following sources such as mining & metallurgy industries, electroplating industries etc. It is a metal of choice for technologists and is an important engineering metal with a wide range of industrial applications such as in copper forming industries, plumbing, electroplating, in manufacture of wires for various industries namely electrical, electronics, automotive, electrical appliances, white goods etc. in alloys such as brass, bronze, gunmetal. Apart from industrial use copper is an necessary trace component required for humans for its function in production of enzyme, bones development But the excessive intake of copper causes headache, nausea and kidney failure and finally gastrointestinal bleeding. United State Environmental Protection Agency has set its Cu^{2+} allowable limits as 1.3 mg/L in industrial waste. World Health Organization (WHO) defines the Cu^{2+}allowable limit of 1.5 mg/L in drinking water. There are many methods which are used for removal of copper from wastewater such as chemical precipitation, ion exchange, membrane filtration, floatation, ultrafiltration, reverse osmosis, electrodialysis, adsorption. Among these techniques, adsorption on naturally available materials is superior to them in terms of cost effectiveness, better removal efficiency even from water containing trace amount of metallic concentration. Currently there are many adsorbents which are used for removing metallic pollutants from aqueous solutions and industrial effluents. Numerous adsorbents like carbon nanotube, activated carbon, modified zeolite, nano adsorbent, Tulsion A-23, Indion GS 300etc are used for the removal of copper from aqueous solution.

1.2 Objective of Project:-

- Aim of the present experimental work is to determine the possibility of utilizing resin for the removal of copper(II) from waste water by adsorption.

- To determine the characteristic of resin Tulsion A-23 for the adsorptive removal of copper by BET Analysis, FTIR Analysis.

- Effect of various factors like pH, amount of adsorbent, contact timetemperature &initial concentration are studied on the removal of copper from water.

- To determine the best fit isotherm equation experimental equilibrium data were fitted to the Langmuir, Freundlich & Temkin isotherm.

- To do kinetic analysis.

CHAPTER 2

LITERATURE REVIEW

2. Literature Review

World Health Organization (WHO) has defined the Cu2+permis-sible limit of 1.5 mg/L in drinking water. Therefore there are numerous technologies which has been adapted to make sure the environmental protection against copper in the industrial discharges. Each technology has its own advantage & disadvantage.

- Chemical Precipitation
- Ion Exchange
- Membrane Filtration
- Electrochemical Methods
- Biological Methods
- Adsorption Methods

2.1 Chemical precipitation:-

This is a ordinarily engaged and predictable process for removing heavy metals from waste-water including copper. It is widely used because of it's its low-priced nature. Pauline[1] reported that the removal efficiencies of copper from wastewater by chemically enhanced primary treatment (CEPT)was found to be 79%. Chen et al[2] determined the removal of copper using precipitation process by lime precipitant. The percentage removal achieved was 99.37%- 99.6% at pH 7-11 respectively.

Ngatenah et al[3] employed precipitation to remove copper from aqueous solution using Groundwater Treatment Plant Sludge (GWTPS).The optimum conditions for 100% removal were found to be pH between pH 2 and pH 2.5, contact time varied from 90 min to 480 min.It is used to treat wastewater which contain high concentrations of heavy metal ions and it is unsuccessful when metal ion concentrations is low..

2.2 Ion Exchange:-

It is another method which is used to remove metal ions from the wastewater. They are either synthetic or natural &have the capability to exchange cations with the wastewater metals...
Selvaraj et al[4] employed ion-exchange process to treat copper containing waste water by Amberjet 1500H and Ambersep 252H resins. They observed from the adsorption isotherm studies that the uptake capacity of Cu (II) on 1500H is larger than that of 252H due to the intrinsic ion exchange capacity, while the adsorbate interaction of 1500H is smaller than that of 252H.Erol and Turkan [5] investigated the removal of copper from aqueous solution by ion - exchange process using using Lewatit CNP 80 resin and Lewatit TP 207 resin.
Doula et al[6] engaged clinoptilolite - Fe system to remove Cu, from drinking water. He found that the system has very large metal adsorption capability and for most of the cases the preserved water models were appropriate for human utilization.Liu and Erhan et al[7] used ion-exchange process to remove copper from aqueous solution by Carboxylate-Containing Resin. The maximum adsorption capability of copper obtained on the resin at pH5.0 was found to be 192 mg/g.

2.3 Membrane Filtration:-

It is a pressure driven separation process for heavy metals which is based on the size elimination and best performance. Nanofiltration, ultra-filtration, electrodialysis and reverse osmosis are some of the examples of the membrane filtration for the effective removal of Cu, Zn, Cd, and Cr from artificial wastewater samples. However, this procedure is not reasonably feasible due to higher preservation and equipped costs. Camarilloa et al[8] employed ultrafiltration technique by polymer enhanced ultrafiltration ceramic membrane to treat copper from wastewater. Yang and Kocherginsky investigated the use of hollow fibre supported liquid membrane (HFSLM) system to remove copper from ammonical waste water.

a) Nanofiltration- Low energy requirements, high efficiency and low cost operation are some of the exceptional settlement which make nanofiltration hopeful technology to remove heavy metal ions. It is a pressure driven membrane process which comes between reverse osmosis and ultrafiltration.

b) Ultrafiltration -. It is an energy demanding procedure, and because of the larger pore size of UF membrane it cannot be used alone rather than dissolved copper ion. This method is important because it has low energy input and this method is considered best for removal of pollutant.

c) Electrodialysis- It is a type of membrane separation process in which the ionized species are passed by applying an electric potential in the aqueous solution.

Tanninen et al[9] studied removal of copper from waste water using Nanofiltration at 0.47 M initial metal concentration. They found the maximum removal up to 96%-98% at 20 bars. Hani and Hassan[10] employed Reverse osmosis and Nanofiltration(NF) technique to remove copper from aqueous solution. From the results they found that the heavy metal's removal efficiency could be achieved by RO process (98%). Through NF, up to 90% of the copper ions were removed. But, this process is not economically feasible due to more continuance and operational expenses.

2.4 Electrochemical Techniques:-

It is electrically accompanied with some other process like ultrafiltration. It is used to remove poisonous heavy metal ions from wastewaters. But it requires relatively large capital investment to start the process supplemented by operational and maintenance costs and the expensive electric supply delimits its applicability.

Akbal and Camcı[11] reported that the removal of copper can be done using Fe- Al electrodes from metal plating industry. They found from the results that at an electrocoagulation time of 20min, a current density of 10mA/cm^2 and at pH 3electrocoagulation with a Fe–Al electrode pair efficiently removed 100% Cu,.0 . Khelifa et al[12] found the optimum conditions for the maximum Cu removal (99%) was pH 6 and current density 0.3A. Chang et al[13] used this process in combination with ultrasound to remove copper from wastewater. They found that the process can successfully remove copper (95.6%) from wastewater.

Escobar et al[14] used electro-coagulation process to remove copper from natural waters and wastewater using electrodes of commercial laminate steel. They determined the optimum conditions for the process as pH 7, flow rate 6.3 cm^3/ min and a current density between 31 A/m^2 and 54 A/m^2But this process is not used because of some drawbacks related with this process like high operating cost, process complication& membrane entangling.

2.5 Biological Methods:-

This is an inexpensive feasible treatment skills for heavy metal removal from wastewater. Narsi et al[15] used the dead biomass of *spirogyra* species, for the removal of copper from aqueous solution. It was observed that the *spirogyra* species shown much better sorption in the pH between 6-7 and at contact time of 30 min. The maximum uptake found was 34.94mg/g.Gupta et al[16] investigated bisorption of copper aqueous solutions by green alga *Spirogyra* species. Hossain and Anantharaman [17] employed bisorption of copper by *Thiobacillus ferrooxidans.* They found the maximum biosorption of copper to be 94.25% within 60 hr of inoculation time with optimum pH 4.5 & temperature 40^0c for 700 ppm initial copper loading.

2.6 Adsorption:-

It is the most common method which is used to remove the heavy metals from waste water that has low concentration of heavy metal. This process produces high quality treated effluent as well as it offers litheness in design & operation. Moreover this it is a reversible process & adsorbents can be renewed by appropriate desorption processes.Various adsorbents like Irish Peat moss, pine cone powder, sugar beet pulp, Indion GS300,Dowex HCR S/S, Dowex Marathon C,1200H, 1500H and IRN97H resins etc have been tested for copper removal.Jaman et al[18] used rice husk as a low cost adsorbent for the removal of copper from wastewater. From the experimental results they observed that almost 90– 98% of the copper could be removed using treated rice husk. They found the results that the adsorption equilibrium data fitted the Langmuir adsorption model very well at different temperatures.

Tariq et al[19] employed adsorption of copper from aqueous solution on to pine fruit a solid adsorbent. From the results they found that the adsorption was pH dependent.The optimum pH for the removal Cu^{+2} was 7.0, the highest adsorption capacity was found to be 14.1 mg of metal ion per gram of adsorbent at initial concentration of 57.6 mg/L of copper ions. The percentage removal was found to be 94.1-96% along the whole range of initial concentrations.

Gaikwad[20] employed adsorption process to remove copper from wastewater using activated carbon derived from coconut shell. From the results he found that the adsorption follows first order kinetics and is slightly endothermic. Yao et al[21] employed batch adsorption studies to remove copper from aqueous solution by chestnut shell.

Besides batch studies, adsorption process is also carried out in different continuous column which helped in scaling up the laboratory data to pilot or industrial scale.

CHAPTER 3

MATERIALS&METHODS

3. Materials & Methods:-

3.1 Adsorbent.

TulsionA-23 resin is a strong base anion exchange resin based on polystyrene matrix, which contains quaternary ammonium Type I group. .It has superb compound and working uniqueness alongside fantastic physical properties because of its split free nature. It is used for a wide range of pH and temperatures. This resin is present in the form of moist sphere-shaped bead in the chloride form with a particle size distribution to provide good kinetics and minimum pressure drop.

Fig 1- Tulsion A-23 Resin

It is used in the field water treatment in hydroxide form along with strong cation exchange resin It is used for a wide range of pH & temperature conditions.

3.2 Adsorbate

All the reagents used were analytical grade chemicals. A stock solution of copper ions (1000 mg/L) was prepared by dissolving 3.929 g of $CuS0_4.5H_20$ in 1000 ml distilled water.

3.3 Apparatus

a) Atomic Absorption Spectrophotometer:

Atomic Absorption Spectrophotometer [Perkin Elnmer, AAS200]was used for the determination of metal concentration in solutions.It is a spectroanalyticalprocess which is used for the quantitative determination of chemical elements employing the absorption of optical radiation (light) by free atoms in the gaseous state. It is used to asses the concentration of an analyte in a sample. It requires standards with known analyte content to establish the relation between the measured absorbance and the analyte concentration and therefore depends on the Beer-Lambert Law.,. Atomic absorption spectrometry has many uses in different areas of chemistry such as:

- Clinical analysis, pharmaceuticals, water analysis:

Fig 2- Atomic Absorption Spectrophotometer

.

b) pH meter.

The pHmeter is an electronic device for measuring the pH (acidity or alkalinity) of a liquid. A typical pH meter consists of a special measuring prod (a glass electrode) connected to an electronic meter that measures and displays the pH reading.

Fig 3- pH meter

c) SHAKER INCUBATOR:-

Shaker incubator(REICO INCUBATOR SHAKER) also known as environmental shaker which is mainly used for cell ventilation & solubility studies. In addition to stable temperature condition, they use an orbital agitation at variable speeds to affect the growth of cell culture.They have adjustable stroke lengths to accommodate various cells and application.

Fig 4-Incubator Shaker

3.4 BET Analysis:-

Brunauer Emmett-Teller(BET) surface analysis is physical adsorption of gas molecules on a solid surface and is used for the determination of the specific surface area of a material. Higher the surface area better is the adsorption behavior of the adsorbent.

3.5 FTIR analysis:-Fourier transforms spectroscopy:-

It is used to determine the functional groups of metal ions or dye ions. It can be applied to a variety of types of spectroscopy including optical spectroscopy, infrared spectroscopy (FTIR, FT-NIRS), nuclear magnetic resonance (NMR) and magnetic resonance spectroscopic imaging (MRSI), mass spectrometry and electron spin resonance spectroscopy.

3.6 Batch Mode Studies:-

The stock solution was diluted to obtain standard solution containing 5-20 mg/L of Cu(II). A100mL of copper solution of any concentration whose pH was adjuste and was taken in conical flask of 250mL capability & known amount of ion exchange resins were added. The pH of the solution was adjusted by using 0.1NHCl or 0.1N NaOH solutions. The solutions were disturbed for a prearranged period at 25^0C in a shaking incubator.The shaking speed was fixed at 120rpm for all the batch experiments. At the end of agitation time resins were filtered and metal content of solutions were analyzed by spectrophotometer[PERKIN ELNMER AAS200]

3.7Isotherm studies:-

These studies were carried out in a 250 mL conical flask. Each flask was filled with 100mL of different initial copper concentration and a fixed amount of resin dosage was added.

After equilibration the solution was separated & analyzed. The initial concentration of solutions taken for the studies were 5, 10, 15,20,25,30 mg/L.

The adsorption capacity was calculated by using following formula:-

$$q_e = \frac{(C_0 - C_{e)}\ V}{m}$$

Whereq_e(mg/g) is the equilibrium adsorption capacity, C_0 &C_e(mg/L) are initial & equilibrium concentration of metal ions in solution, V(L) is the volume, & the m(g) is the amount of the resin.

3.7 <u>Kinetic studies</u>

This experiment was carried out by using a known weight of resin dosage and Cu(II) concentration was varied in the range of 5-20 mg/L. The samples at different time intervals (0-60 min) were taken and remaining metal concentrations were analyzed. The rate constants were calculated using rate expressions. This formula was used to determine adsorbed metal concentration.

$$q_t = \frac{(C_{0-}C_t)V}{m}$$

Where q_t(mg/g) is the adsorption capacity at time t, C_0(mg/L) is the initial metal concentration, C_t(mg/L) is the concentration of metal ions solution at time(t),V(L) is the volume & (mg) is the amount of resin.

CHAPTER 4

RESULTS & DISCUSSIONS

4.1 Discussion on Characteristic of resin:-

i) BET Analysis: - BET surface area of resin Tulsion A-23 was found to be 5.492 m^2/g and total pore volume as 5.286E-01 cc/g using BET analyzer [Autosorb 1A, Quantachrome Instruments].

ii) FTIR Analysis: This procedure is used to identify some characteristic functional groups which adsorbs metal ions and dye ions. The figure below represents

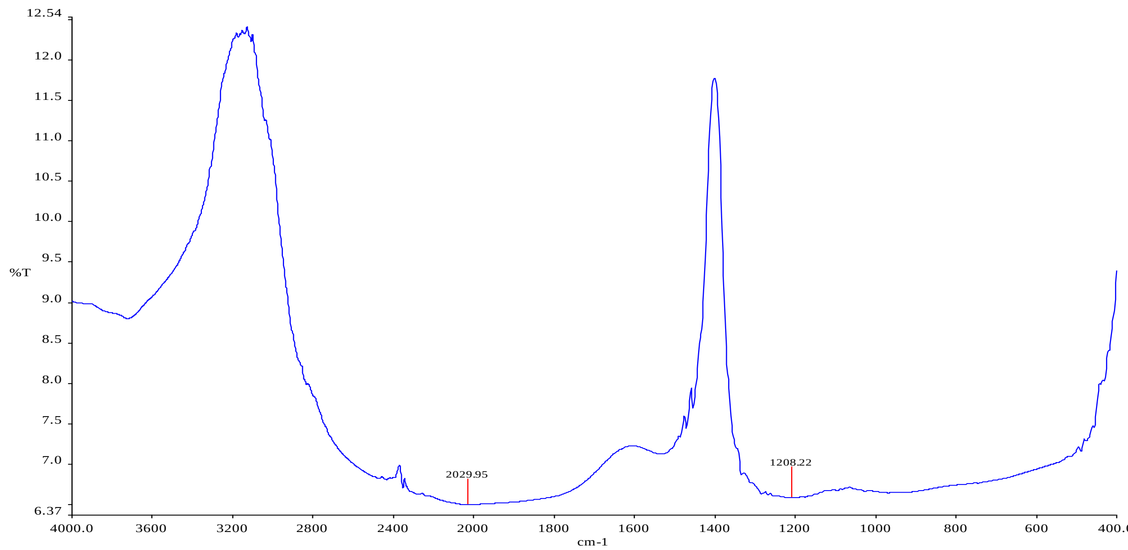

FIG 5- Ftir Analysis ofTulsion A-23 Resin Before Adsorption

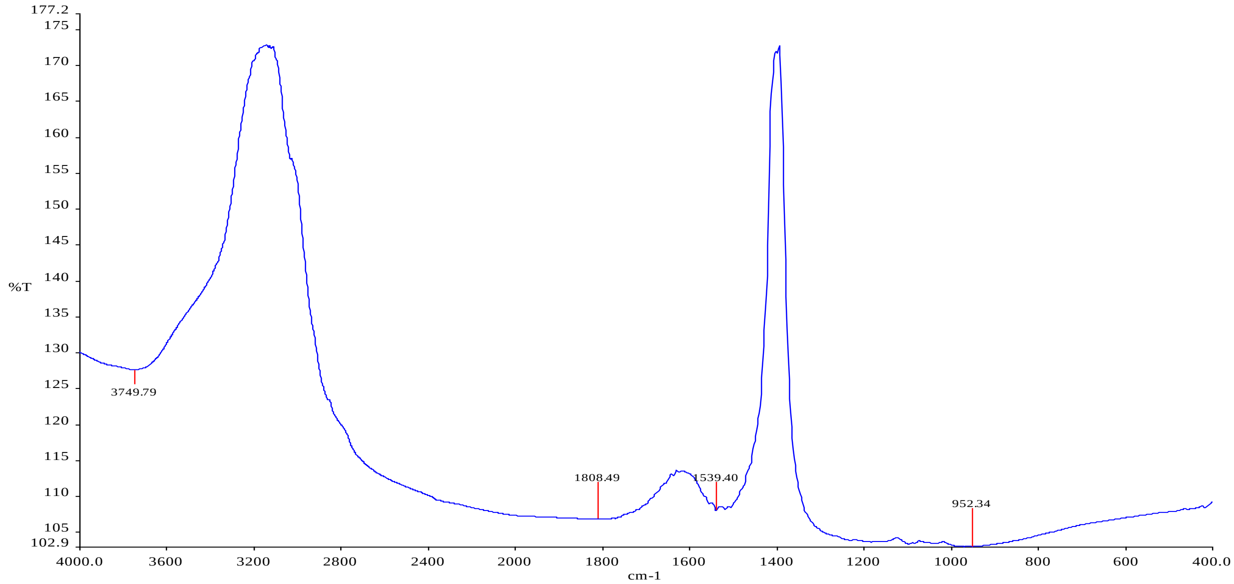

FIG 6-   FTIR Analysis of Tulsion resinA-23 after adsorption

Table:-I

Serial No.	Compound Type	Frequency
1	0-C(2 bands) str	1208.22
2	–N=C=O,-N=C=S, -N=C=N-,-N_3,C=C=O	2029.95
3	=C-H & CH_2	952.34
4	N-H med(2i amide) II band	1505.49
5	C-H(aldehyde C-H) med	2749.79

4.2) ADSORPTION STUDY ON EFFECT OF VARIOUS PARAMETERS:-

4.2.1) Effect of contact time on removal of copper(II):-

Itis an essential parameter to determine the economical practicality of contaminant removal from wastewater. The effect of contact time on adsorption of Cu(II) on Tulsion A-23 resin was investigated by conducting batch experiments at various time upto 120 min. The experimental conditions were maintained at initial concentration of 10ppm,pH 7.16,agitation speed 130 rpm and amount of adsorbent is 1.5g/L. The experimental results showed that the removal of copper(II)increased sharply during first 60 min and after that equilibrium is reached and no significant removal of copper was observed. After 90min the adsorption rate became practically slow & it started decreasing. The difference in degree of adsorption may be due to the fact that in the beginning allthe sites on the surface of adsorbent were vacant. Therefore the extent of copper removal decreased with increase in contact time due to decrease in avaibility of active sites for adsorption. Based on these results 90 min is considered as optimum time for rest of the experiments.

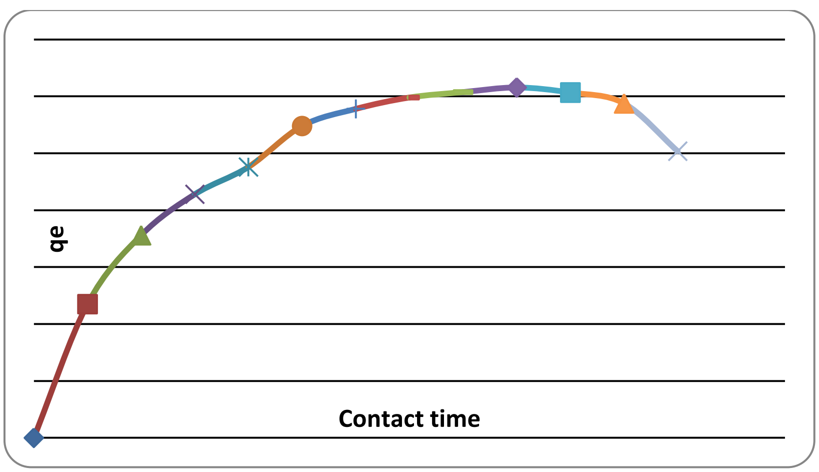

Fig 7- Effect of contact time on copper removal

4.2.2 Effect of pH:-

The ion exchange process is mainly affected by hydronium ion concentration and the ionization of surface functional groups is influenced by the solution pH. A change in pH not only moulds the surface charge on the adsorbent but also alters solution chemistry of heavy metals: hydrolysis, redox reaction, degree of ionization, precipitation and specification of heavy metals, which apparently affect the adsorption process. The effect of pH on the removal of copper on the adsorption of copper was studied at 25^0C, initial metal concentration 10ppm,adsorbent dose 1.5g/L by varying the pH of metal solution from 2-12.The maximum adsorption was observed within the pH range 5-7 which is due to partial hydrolysis of metal ions. Further increase in pH ie above 8 causes precipitation of copper ions on the surface of adsorbent by nucleation. Thus from the results it was clear that at pH the metal uptake was more so pH 7.45 was taken as optimum pH for rest of the experiments.

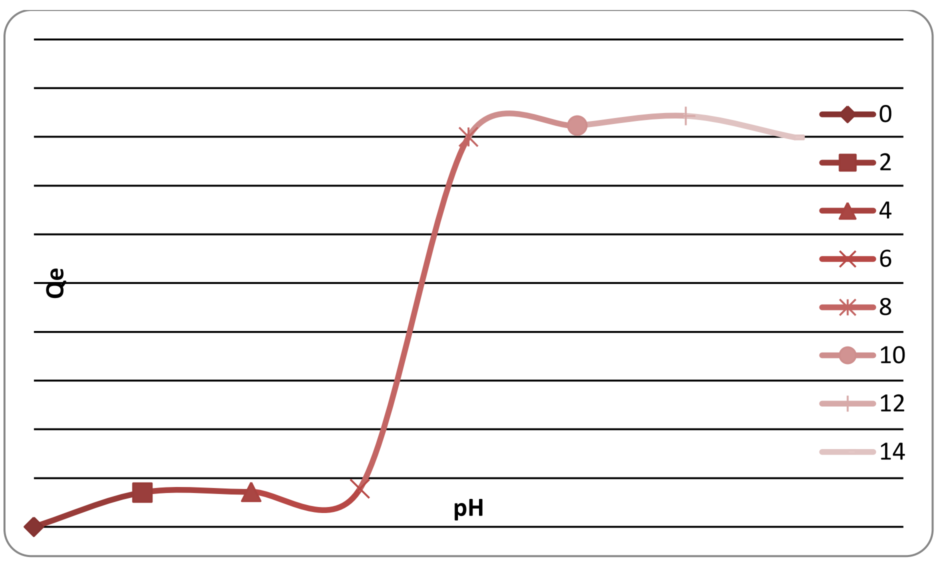

Fig 8- Effect of pH on removal of copper from solution

4.2.3 <u>Effect of adsorbent dose</u>:-

The effect of variation of resin dosage on the removal of copper by tulsion A-23 are shown in fig-- below. Resin dosage was varied from 1 to 3g and equilibrated for 90 min at an initial copper concentration of 10mg/L and pH optimization taken as 7.46. Percentage removal increases with increasing amount of resin. When the adsorbent dose increases, the number of active surface for adsorption will increase and this ultimately results in increase of the percentage of Cu(II) removal from the solution. Increasing trend of removal of Cu(II) is due to availability of greater active surface for adsorption. It was observed that on further raising the dose, removal did not increase which was due to higher number of unsaturated adsorption sites Fromfig 9 it is apparent that for the quantative removal of 10mg/L copper, a minimum resin dosage of 1g is required.

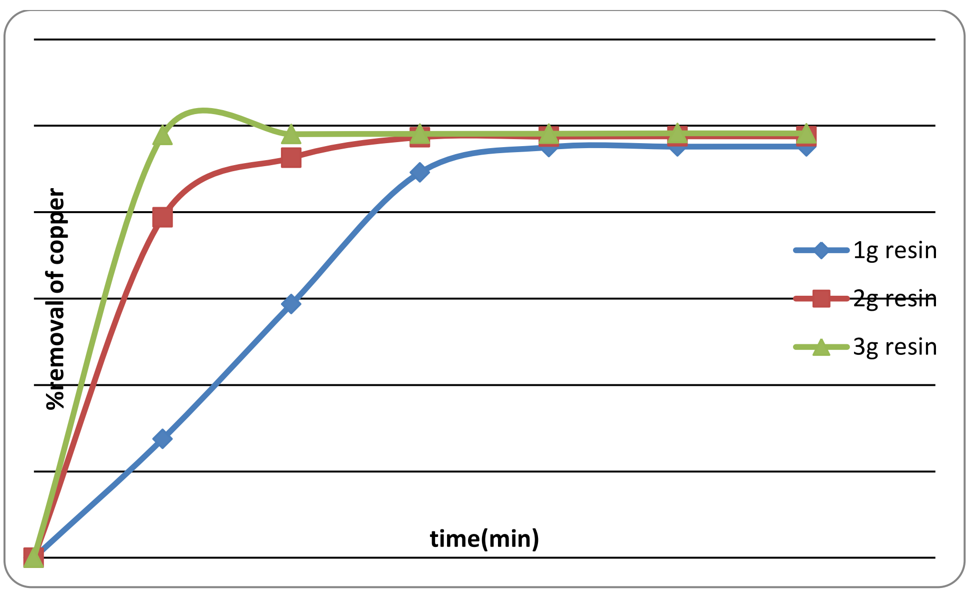

Fig 9- Effect of dose of adsorbent on copper removal

4.2.4 Effect of initial metal concentration:-

Removal of Copper for various initial concentrations (10 to 70 mg/L) by resin (1g/L) at 130 min contact time and at pH 6.86 has been depicted in the Fig X. The percentage copper adsorbed increased 96.65% to 98.3% with increase in initial concentration from 10mg/L to 70mg/L. More adsorption at higher initial metal concentration may be responsible for increasing percentage removal at increasing initial metal concentration. It reflects that the resistance to mass transfer reduces therefore the removal decreases at higher metal concentration. Based on the experimental values, 50mg/L Copper concentration is selected as the optimized value for further use.

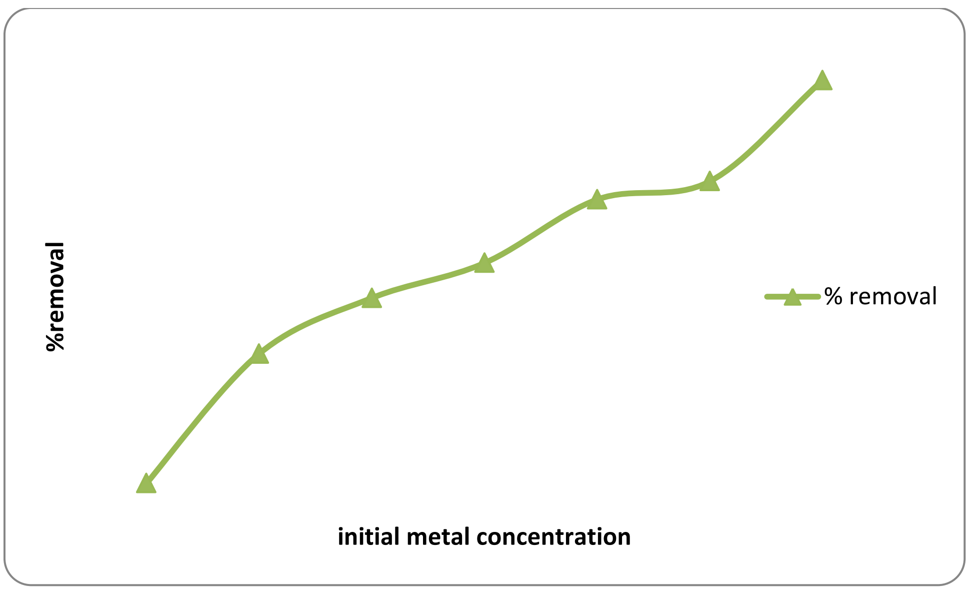

Fig 10- Effect of Initial metal concentration on removal of copper

4.2.5 **<u>Effect of temperature</u>:-**

Temperature determines whether the adsorption process is favourable at higher temperature or at lower temperature. A temperature supplies energy to the system in the form of heat and affects the adsorption capacity depending on the exothermic or endothermic nature of the system. Experiments were conducted at three different temperatures. Removal of copper increased with increase in temperature which means that adsorbate-adsorbent system follows endothermic process. The rise of adsorption capability with rise of temperature was attributed due to increase of surface active sites available for adsorption of copper ions. Thus in this figure the uptake capacity of copper increases for the temperature range of 25^0C to 32^0C.Thus removal increases at higher temperature because of dissociation of functional groups present on the adsorbent surface.

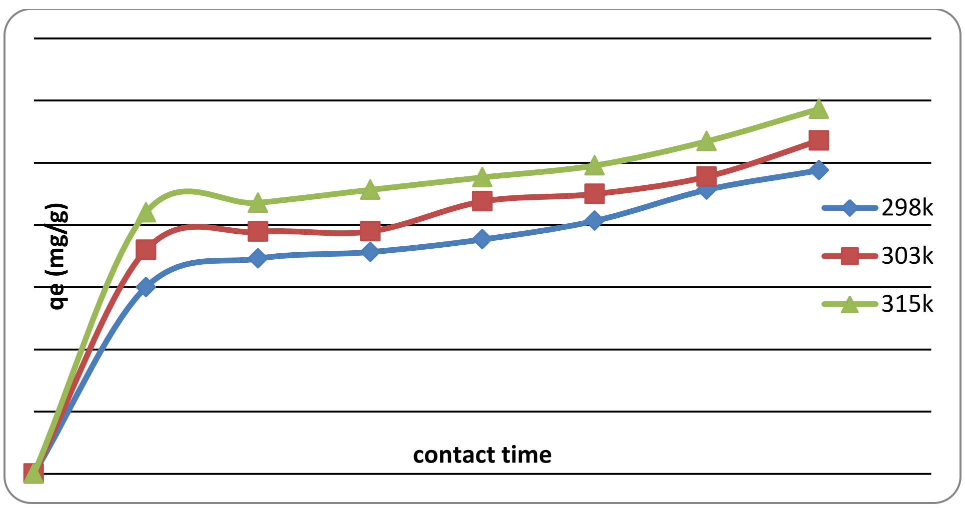

Fig 11-Effect of temp on removal of copper

4.2.6 ADSORPTION ISOTHERMS:-

An adsorption isotherm describes the relationship between the amount of adsorbate on the adsorbent and the concentration of dissolved adsorbate in the liquid phase at equilibrium. Freundlich, Langmuir&Temkin isotherms are the most commonly used to describe the adsorption characteristics of adsorbents used in water and wastewater

a) <u>Langmuir Isotherm Model:-</u>

This model describes the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption will take place. This model represents the equilibrium distribution of metal ions between the solid and liquid phases. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of similar sites. Based upon these above reasons, Langmuir represented the following equation:

$$\frac{1}{q_e} = \frac{1}{Q_0\, b}\frac{1}{C_e} + \frac{1}{Q_0}$$

Where,

q_e= the amount of copper adsorbed per unit weight of the adsorbent (mg/g),

Ce= the equilibrium concentration of copper in solution (mg/L),

Q_o= the amount of adsorbate at complete monolayer coverage (mg/g)

b = Langmuir isotherm constant that relates to the energy of adsorption(L/mg)

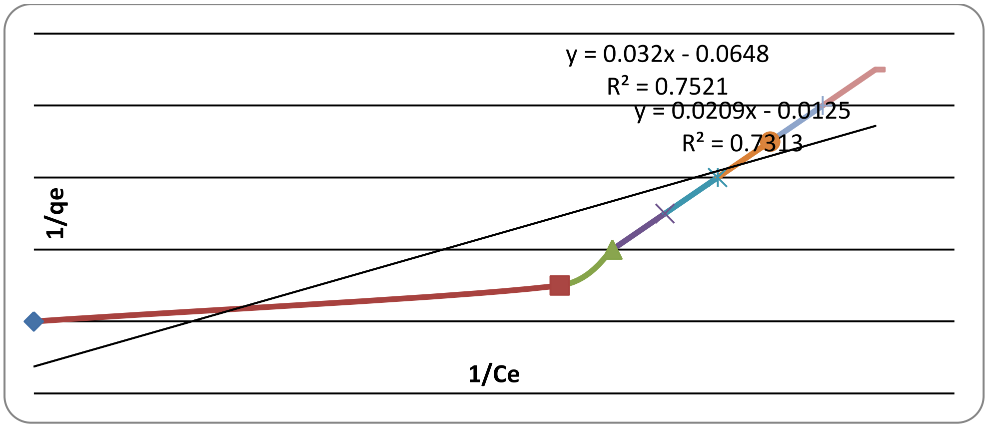

Fig 12- Langmuir adsorption Isotherm for Cu on Tulsion A-23

The values of Qo and b were computed from the slope and intercept of the Langmuir plot of $1/q_e$ versus $1/C_e$.

b) Freundlich isotherm model:-

This model describes the characteristics of adsorption for the multilayered surface.The Freundlich equation is given by:

$$q_e = K_F {C_e}^{1/n}$$

Where Kf= Freundlich isotherm constant (mg/g)

n = adsorption intensity;

Ce= the equilibrium concentration of adsorbate (mg/L)

qe= the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g).

Linearizing the above equation

$$log q_e = log K_F + \frac{1}{n} \log C_e$$

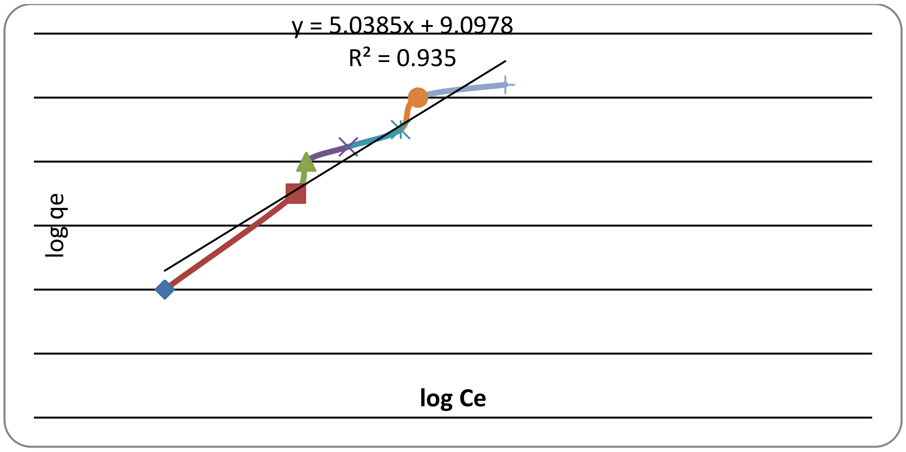

Fig 13:-Freundlich Adsorption Isotherm for Cu on Tulsion A-23

The constant K_f is an approximate indicator of adsorption capacity,If n lies between one and ten, this indicates a favorable sorption process.

c) Temkin Isotherm Model:-

This isotherm deals with adsorbent–adsorbate interactions. This model assumed that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage. Here the graph is plotted between qe against lnCe and the constants were determined from the slope and intercept. The model is given by the following equation

$$q_e = \frac{RT}{B} \ln(aC_e)$$

Linear form of temkin isotherm is given by

$$q_e = a + b\ lnC_e$$

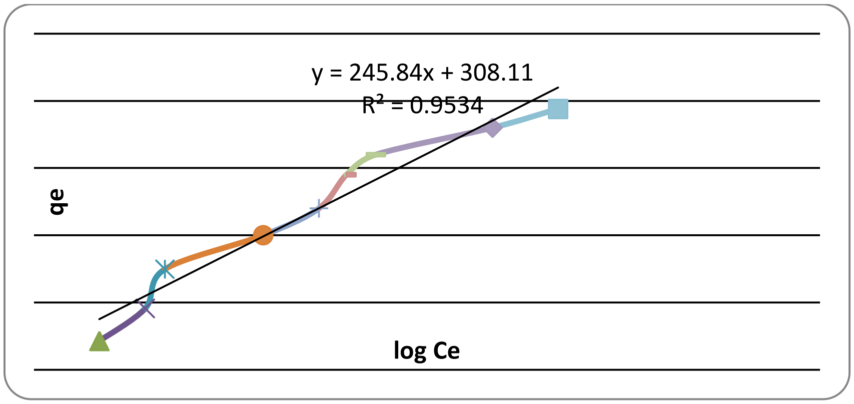

Fig 14:- Temkin Adsorption Isotherm for Cu on Tulsion A-23

Table II Langmuir, Freundlich, Temkin Isotherms:-

Temperature	Langmuir			Freundlich			Temkin		
	Q_0	b	R^2	n	log K_F	R^2	a	b	R^2
298 K	-15.43	-2.02	0.7521	0.2	9.0327	0.935	452.6	389.49	0.953

TABLE-III

Comparison of adsorption capacity with other resins:-

Resins	Adsorption Capacity(mg/g)	Reference
252H & 1500H	40.65	Kim et al[23]
Dowex HCR S/S	15.64	Veli [24]
Present work	20.56	

4.2.7 Kinetics analysis:-

The pseudo-first order, pseudo second order models are all tested to determine the adsorption kinetics.

a) ***Pseudo-first order model:-***

The linearized form of the pseudo-first order model is written as

$$\frac{dq}{dt} = K_1(q_e - q_t)$$

After integration the equation becomes

$$\log(q_e - q_t) = log q_e - \left(\frac{K_1}{2.303}\right)t$$

where K_1 (min^{-1}) is the first order rate constant, q_e and q_t are the amount of adsorbate species adsorbed on adsorbent at equilibrium and at any time, respectively. The values of K_1 at different temperatures were calculated by retrieving slope via plotting a graph between 'log(qe-q) vs t' at different temperatures. The values of the rate constants of pseudo first and pseudo second order kinetic models at different temperatures are tabulated

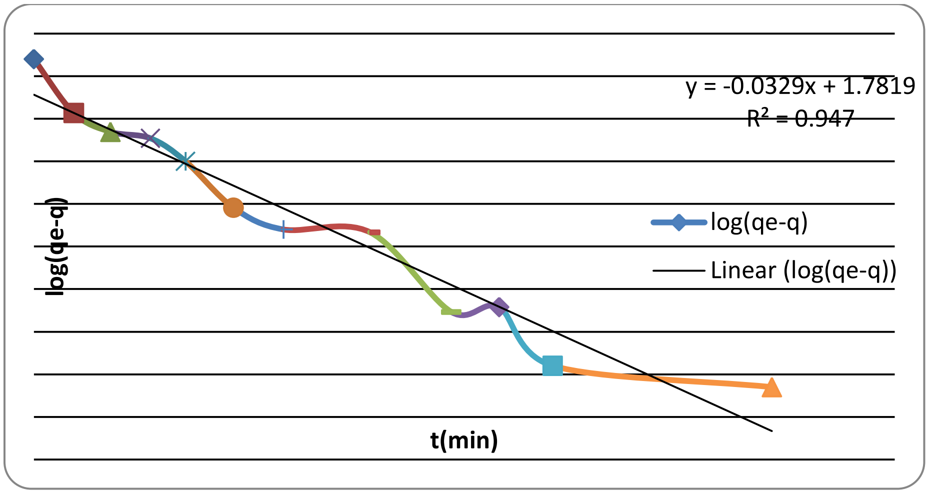

Fig15:- 1st order rate kinetics

b) Pseudo-second order model:-

Resultant data were also tested for pseudo second order kinetic model. It is based on the assumption that rate limiting step is chemisorption in nature. The pseudo second order equation is given by

$$\frac{dq}{dt} = K_2(q_e - q_t)^2$$

whereK_2(g $mg^{-1}min^{-1}$) is the rate constant for pseudo second order model equation. Above mentioned equation can be written as

$$\frac{t}{q_t} = \frac{1}{K_2{q_e}^2} + \frac{t}{q_e}$$

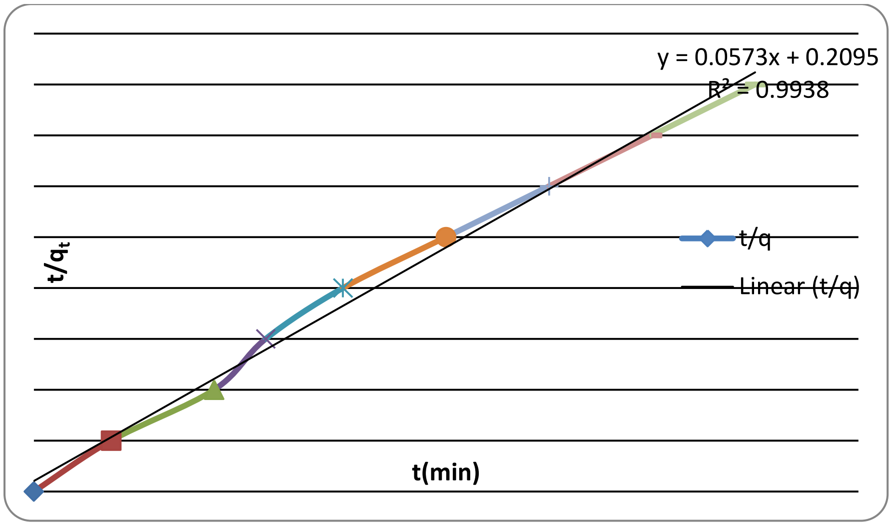

Fig 16:- 2nd order rate kinetics

Table-IV

1st order kinetics		2nd order kinetics	
K_1	R^2	K_2	R^2
0.053	0.947	0.0068	0.993

On comparing the values of correlation coefficients (R^2) it is proximate that the kinetic data is better fitted in second order model as compared with the first order model.

CHAPTER 5

CONCLUSIONS

5.1 Conclusions:-

- In this study ion exchange resin(Tulsion A-23) has been identified as efficient material which is capable of removing copper from the aqueous solution to the extent of 98.3% at the solution pH of 6.86.
- From BET Analysis the surface area of resin is found to be 5.492m^2/g and total pore volume is 0.05286 cc/g.
- The minimum resin dose required for removal was found to be 1g at pH 6.86.The contact time required for batch process was 90 min at 25^0c temperature & 130 rpm.
- The adsorption process obeys the Temkin adsorption isotherm very closely. There was no desorption upto 90min which indicated that the adsorbed copper remains almost stable on resins.
- The results also demonstrate that the process follows second order rate kinetics with k=0.0068.

5.2 Future Scope of Work: -

According to the results obtained for the removal of copper, the resin named TULSION A-23 can be used for the removal of other metals also like zinc, cadmium, chromium etc. Experiments can be performed for these metals also to see how much effective this resin is for the removal of other metals. The regeneration studies can also be done for the resin so that it can be used again and again giving higher efficiency in comparison to single cycle.

CHAPTER 6

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